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ELEMENTAL SULFUR CORROSION OF MILD STEEL AT HIGH CONCENTRATIONS OF SODIUM CHLORIDE

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ABSTRACT

Elemental sulfur deposition commonly occurs in sour gas production fields, especially in high H_2S concentration level reservoirs. In aqueous conditions, contact of solid sulfur with mild steel can initiate catastrophic corrosion problems. According to the previous research, in the presence of high concentration of salt, the corrosion process may be dramatically accelerated.

The objective of this project is to study the effect of high sodium chloride concentration on elemental sulfur corrosion of mild steel. Sulfur-mild steel corrosion at both salt free and 10 wt. % sodium chloride conditions was investigated. Severe corrosion attack to the steel was found in both of the studied conditions. Iron sulfide films/scales readily formed on the surface of the steel. These were analyzed by infinite focus microscopy (IFM), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Corrosion products were mostly generated in the periphery area of sulfur pellet at the high salt concentration conditions, which is different from the observation at salt free conditions. It was also found that an increase of salt concentration significantly increases the uniform corrosion rate, as well as the localized corrosion rate.

Keywords: Elemental sulfur, mild steel, high sodium chloride concentration, iron sulfide, localized corrosion.

INTRODUCTION

Elemental sulfur deposition has become a major concern in the sour gas production industry. The precipitation of sulfur in the flow lines can cause the diminishing of oil and gas transportation efficiency, and finally if left unchecked may block the flow lines. Simultaneously, the direct contact between carbon steel and wet elemental sulfur can cause a severe corrosion problem.

Studies on elemental sulfur corrosion date from the 1970s[1]. The fact that wet elemental sulfur can cause sever attack to the carbon steel has been well established. However, the mechanism of sulfur corrosion is still poorly understood. Acidification in sulfur containing aqueous systems has been reported, with species such as H_2S, H_2SO_2, H_2SO_3, H_2SO_4 and polysulfides being possible candidates as hydrolysis products.[2] Maldonado-Zagal and Boden[3] proposed that acid formation as a result of sulfur hydrolysis was the main factor governing corrosion in the presence of elemental sulfur:

$$S_8 \text{ (s)} + 8\,H_2O \text{ (l)} \rightarrow 6\,H_2S \text{ (aq)} + 2\,H_2SO_4 \text{ (aq)} \tag{1}$$

MacDonald *et al.* hypothesized that an electrochemical reaction between iron and polysulfide is the driving force for corrosion in systems where elemental sulfur is present[1].

$$(x\text{-}1)Fe + S_{y\text{-}1}{\cdot}S^{2-} + 2\,H^+ \rightarrow (x\text{-}1)FeS + H_2S + S_{y\text{-}x} \tag{2}$$
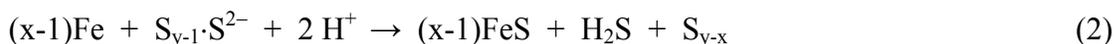
Alternatively, another electrochemical mechanism for wet elemental sulfur corrosion was proposed by G. Schmitt in 1991[4]. Sulfide-catalyzed cathodic sulfur reduction was believed to be the most important step:

$$[FeS_{x+1}] + 2e^- \rightarrow [FeS_x] + S^{2-} \tag{3}$$

Direct contact between sulfur and steel is necessary to make the reaction happen. Iron sulfide film plays an important role in the corrosion process.

Following the previous researches, a preliminary experiment has been conducted and reported[5]. In that study, elemental sulfur hydrolysis and sulfur-mild steel corrosion have been investigated under salt free conditions. Sulfur was found to react with water at temperatures of greater than 80°C, resulting in slight acidification of the corrosion solutions. The stabilized pH values measured were significantly higher than those reported in a similar study by Maldonado-Zagal and Boden[1]. Also, it is unclear if this mechanism can be used as an explanation for localized attack on mild steel by elemental sulfur, given that the lowest pH values observed fall within the typical pH range observed in water/CO_2 systems.

Experimental results also showed that steel was corroded severely when it has a direct contact with wet elemental sulfur at salt free conditions. The general corrosion rate is up to 1 mm/yr, even at ambient temperature. Localized pitting rates up to 7 mm/yr were observed. It is worth noting that the thick deposits of iron sulfide on the steel substrate formed directly beneath the elemental sulfur. It was also observed that part of the films imprinted the polishing marks. Consequently, it was proposed that a direct solid-state reaction for the formation of iron sulfide from elemental precursors is a more likely process which may occur in the system:

$$8\,Fe \text{ (s.)} + S_8 \text{ (s.)} \rightarrow 8\,FeS \text{ (s.)} \tag{4}$$

However, because of the complicated nature of elemental sulfur, there may be more reactions present in the corrosion process.

High salt concentration effects on elemental sulfur corrosion have been investigated by Dowling in 1987[6] and Schmitt in 1991[4]. According to their observations, an increase of salt concentration significantly increases the corrosion rate; in another words, salt worsens elemental sulfur corrosion.

However, based on Fang's previous research[7,8], high salt concentrations retard both uniform CO_2 and H_2S corrosion. Therefore, it is necessary to further investigate the high salt concentration effect on elemental sulfur corrosion. This will also be helpful for the elucidation of the elemental sulfur corrosion mechanism.

The overall objective of this project is to study the effect of elemental sulfur on the corrosion of mild steel, with particular emphasis on detection of pH effects, identification of formed corrosion products, study of pitting phenomena and measurement of general/localized corrosion rates.

EXPERIMENTAL PROCEDURE

Carbon-steel 1018 (C1018) coupons were used in the experiments. Specimens were polished with silicon carbide sand paper prior to being tested. The sand paper grit number was used in the following order: 240, 400, 600. After polishing, specimens were immersed in isopropyl alcohol in an ultrasonic cleaner for 1 to 2 minutes, then air dried. After coupon polishing, elemental sulfur (ACROS 99.999%) was deposited onto polished coupons by heating it slightly above its melting-point (115°C) then pouring it onto the coupon surface (C1018 steel). This gave uniform coverage of adherent sulfur to the coupon surface. Care was taken not to oxidize the sulfur as it was heated.

Coupons thus prepared were then transferred to a glass cell for corrosion experiments. Conditions for the elemental sulfur corrosion experiments are summarized in the test matrix outlined in Table 1.

Corrosion coupons were removed from the glass cell and characterized after 1, 4 and 5 days. Prior to analysis, unreacted sulfur was mechanically removed from the coupon surface, which caused partial loss of the corrosion product. Samples were characterized with a JEOL6390LV scanning electron microscope (SEM), EDAX energy dispersive X-ray fluorescence attachment (EDX), and Alicona infinite focus microscope (IFM). Corrosion products were then removed by treatment with Clarke solution, ASTM standard G1 section 7.7.2 approved by ASTM committee April 24 1981, and the corrosion coupon surface was imaged by IFM. Localized corrosion rates were determined by analysis of IFM data whereas general corrosion rates were obtained by weight loss methods.

RESULTS AND DISCUSSION

Coupons with elemental sulfur on the surface before and after 1, 4 and 5 days exposure at 25°C are shown in Figure 1,

Figure 2 and Figure 3. Interestingly, a black iron sulfide film was formed on the coupon area which has no direct contact with elemental sulfur. This is quite different from what has been observed in salt free conditions, where only the portion of coupon surface underneath the sulfur was significantly blackened after exposure. Detailed comparisons of experimental results between salt free and high salt concentration conditions will be shown later.

Representative SEM/EDX data for the corrosion coupon surface that has been in direct contact with elemental sulfur for one day at 25°C is shown in Figure 4. The red circled area represents the area that was covered by the sulfur pellet. Most film generation occurred in close proximity to the periphery of the sulfur pellet. This phenomenon confirms the observation made by Smith in 1990[9]. A further

enlargement of the small area underneath the sulfur pellet (top right) shows clear polishing marks covered by small quantity of corrosion product. A high magnification SEM picture shows the outer area which was uncovered by sulfur, a much thicker film was generated in this area. The composition of the film was shown by EDX to consist of iron sulfide. The IFM image of the corrosion coupon after the iron sulfide has been removed reveals severe localized corrosion in the outer area (Figure 5). The top right and bottom left images correspond to the small regions marked on the "whole coupon" picture. The line across the top right of the image corresponds to the profile data of the coupon surface. IFM data show that the coupon surface beneath the sulfur pellet was barely corroded. Comparison with the SEM pictures of coupon surface with film reveals that the steel corrodes more severely when more film is generated on the coupon surface. After four days at 25°C a thicker film has formed at both the inner and outer surface, see Figure 6. However, the film on the outer coupon surface is still much thicker than the film on the inner coupon surface. Cracking of the film is observed on the coupon surface. From EDX, it is clear that the film chemistry remains fundamentally unchanged with longer exposure. IFM data, Figure 7, indicates that several shallow holes start to form on the sulfur covered region. This is indicative of initiation of pitting corrosion. Localized corrosion attack on the outer coupon surface is still significant. The corrosion depth is about 25 μm and it increases with time. After a 5 day exposure at 25°C, see Figure 8, the films seem to be even thicker and coarser than before. However, the polishing marks are still observable in the region which was covered by elemental sulfur. IFM data, Figure 9, show that the shallow pits generated at the fourth day continue to grow. The outer surface also shows greater localized corrosion depth.

A similar series of experiments was conducted at 80°C. Coupons with elemental sulfur on the surface before and after 1, 4 and 5 days exposure at 80°C are shown in Figure 10, Figure 11 and Figure 12. Similar to the experimental results at 25°C, the corrosion product films appeared to be all over the coupon surface.

After one day at 80°C there is a much thicker film present on the coupon surface than was observed at 25°C, see Figure 13. The white regions of the image are caused by deposition of sodium chloride. The thickness and macroporosity of film makes it difficult to completely dissolve the salt from the coupon surface. IFM data, Figure 14, of the coupon surface after film removal clearly shows a much more severe localized corrosion attack. Interestingly, in the region of the sulfur covered surface, part of the steel was corroded away yet another region of the coupon surface remained with the original appearance (polishing marks visible). The localized corrosion depth around the outer surface is around 55 μm, representing a 20 mm/yr corrosion rate. This is an extremely high corrosion rate. After 4 days at 80°C, Figure 15, the film has become thicker and coarser. After 5 days at 80°C, Figure 16, the entire surface seems to be covered by a coarse and cracked film. The films appear to be much denser and highly crystalline. IFM data show the coupon surface after film removal. A layer of the original steel surface was corroded away. It is difficult to quantify the localized corrosion depth because the original coupon surface is gone. However, a surface profile analysis is still given for reference. The depth is around 35μm. It was noted that the corrosion rate decreased with time.

Figure 19 shows the comparison of general corrosion rates between salt free and 10 wt.% NaCl conditions at 25°C. Results clearly indicate that an increase of salt concentration significantly increases the general elemental sulfur corrosion rates. General corrosion rates increased two to three times when salt concentration was increased from 0 wt.% to 10 wt.% at 25°C. Another significant difference between the experimental results at salt free and high salt concentration conditions is the nature of film formation. From Figure 18, it is seen that the thick deposits of iron sulfide on the steel substrate formed

directly beneath the elemental sulfur at salt free conditions. However, at high salt concentration, most of the corrosion product films were generated in the region which is not covered by elemental sulfur. Similar observations of film formation were first reported by Smith[9]. Hydrogen polysulfide formed by hydrogen sulfide and elemental sulfur at the periphery of the sulfur pellet was suggested to explain these phenomena. However, in the present experiments, no H_2S is added into the system, which is different from Smith's experiments. Therefore, other scenarios need to be investigated to further explain the observed phenomena.

As stated above, the direct solid-state reaction mechanism proposed before is unlikely to be the sole process during elemental sulfur corrosion. The differences in film formation at different salt concentrations suggest that a high concentration of salt plays an important role in the elemental sulfur corrosion process. How exactly high concentrations of salt affect elemental sulfur corrosion will be the subject of future investigations.

CONCLUSIONS

- High salt concentrations significantly increase the overall general corrosion rate of carbon steel in the presence of elemental sulfur.
- Corrosion products were mostly generated at the periphery of the sulfur pellet at the condition of high salt concentration.
- How high concentration of chloride affects elemental sulfur corrosion needs to be further investigated.

ACKNOWLEDGEMENTS

TABLE

Table 1.
TEST MATRIX FOR ELEMENTAL SULFUR CORROSION EXPERIMENTS

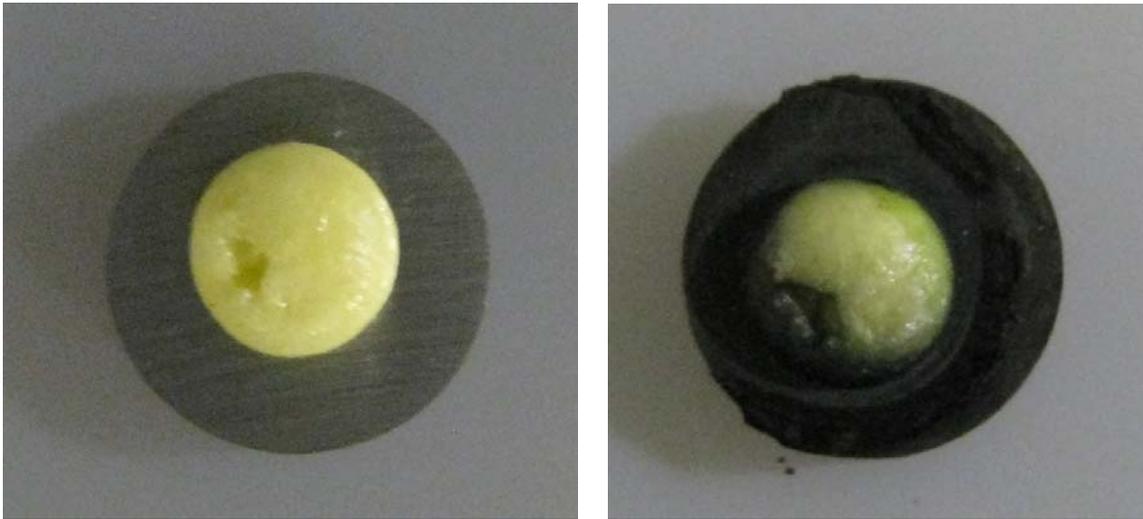| Parameter	Conditions
Total Pressure	1 bar
Temperature	25, 80ºC
Solution	10 wt. % NaCl
Initial pH	7.0
Material	C1018

FIGURES

Figure 1. Corrosion coupon before and after 1 day exposure at 25°C.

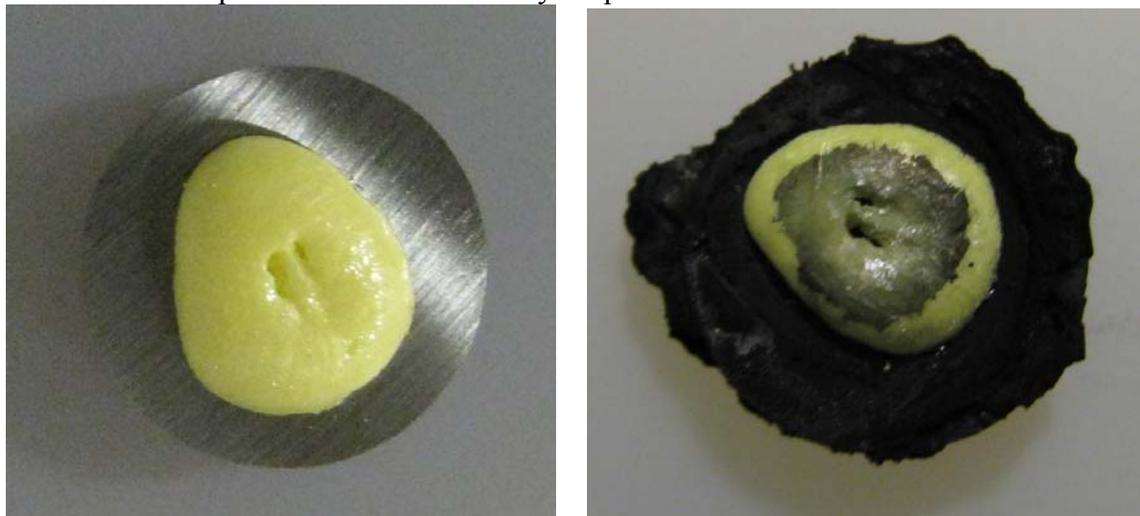Figure 2. Corrosion coupon before and after 4 days exposure at 25°C.

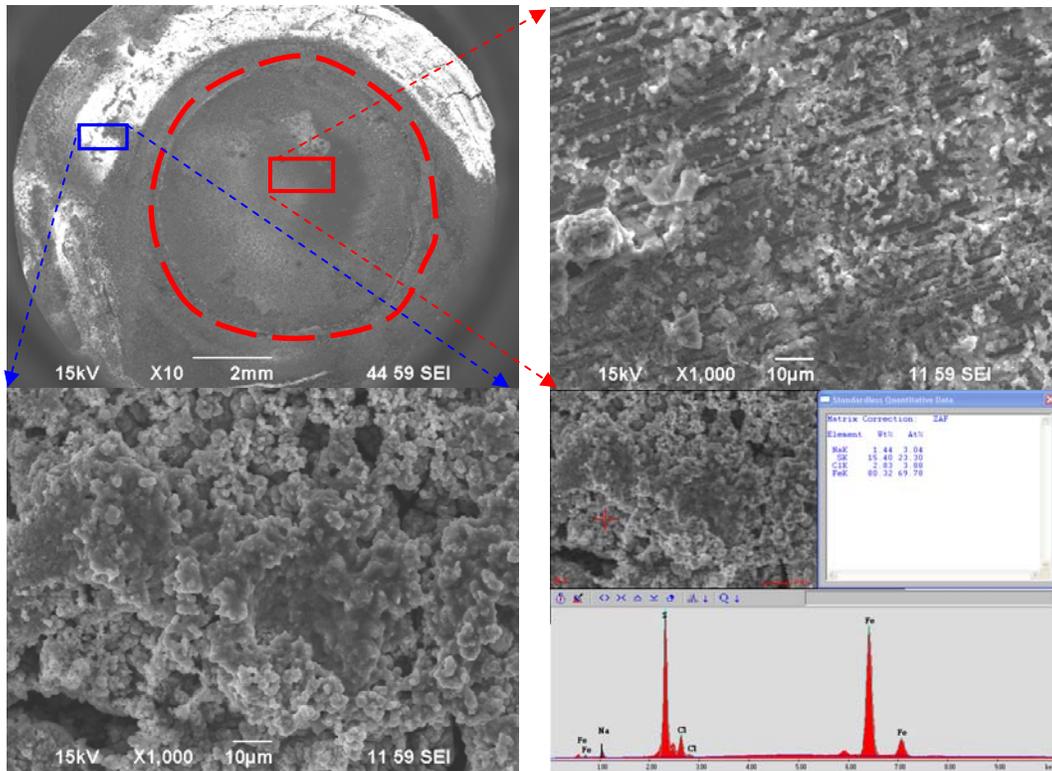Figure 3. Corrosion coupon before and after 5 days exposure at 25°C.

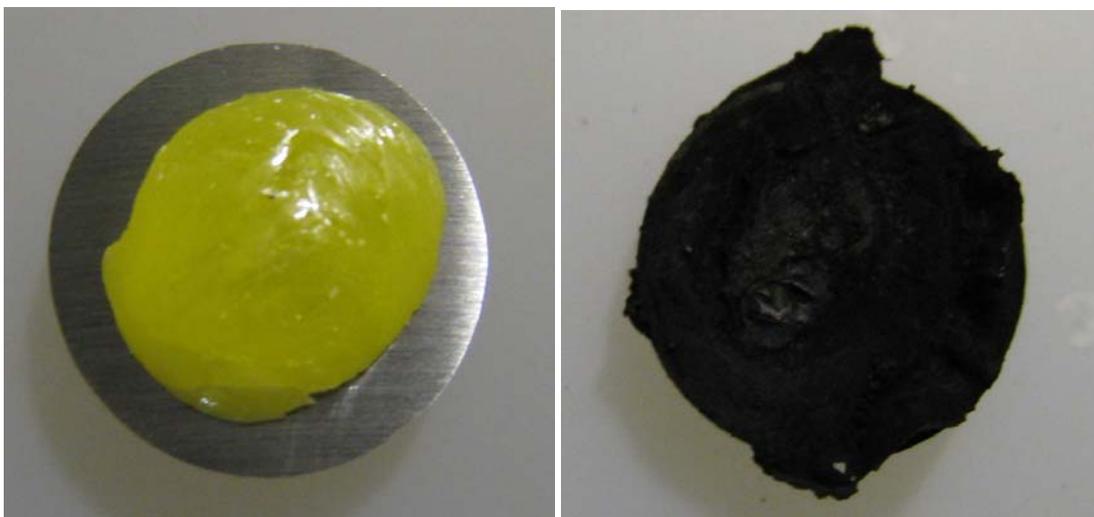Figure 4. Corrosion coupon contacted with elemental sulfur for 1 day at 25°C, with film.
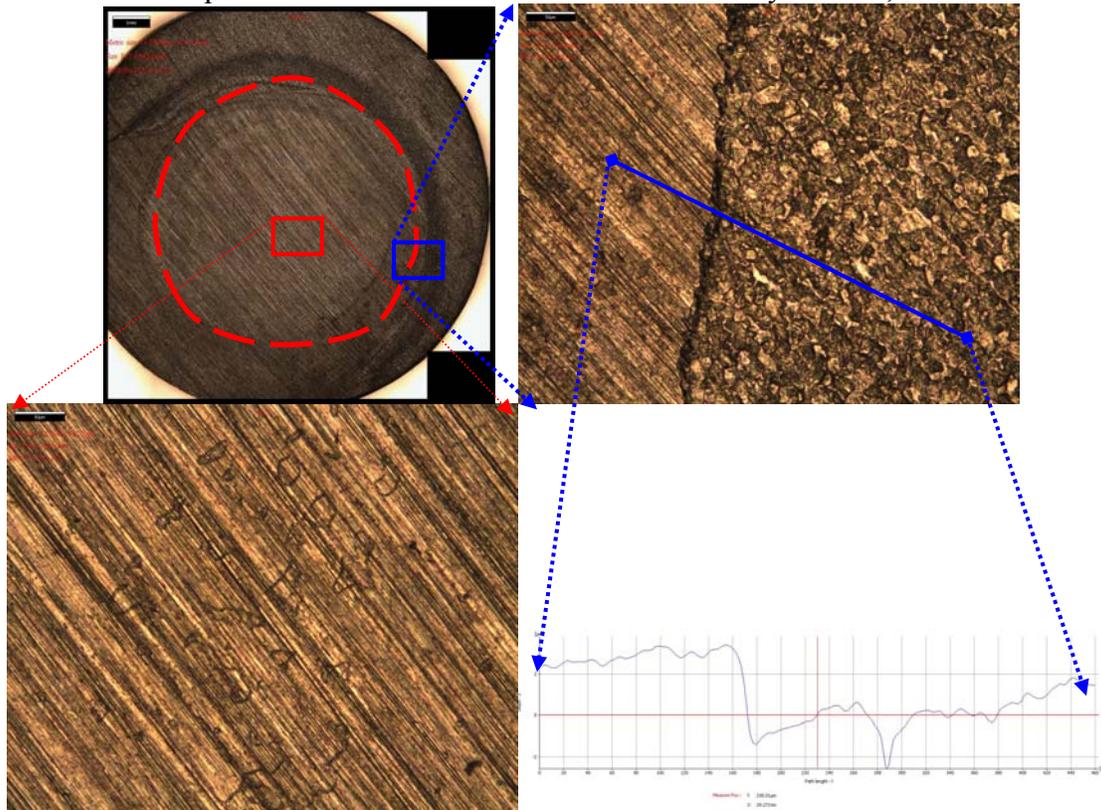
Figure 5. IFM data for corrosion coupon for 1 day at 25°C, without film, appearance of the surface and a line profile.
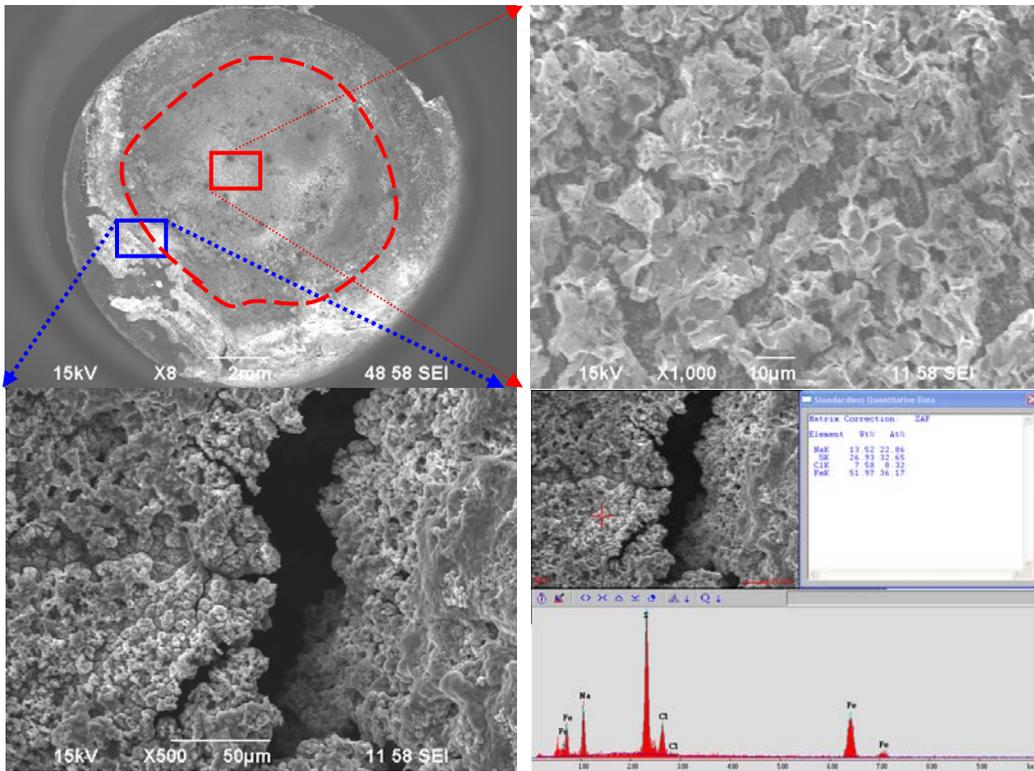
Figure 6. Corrosion coupon contacted with elemental sulfur for 4 days at 25°C, with film.
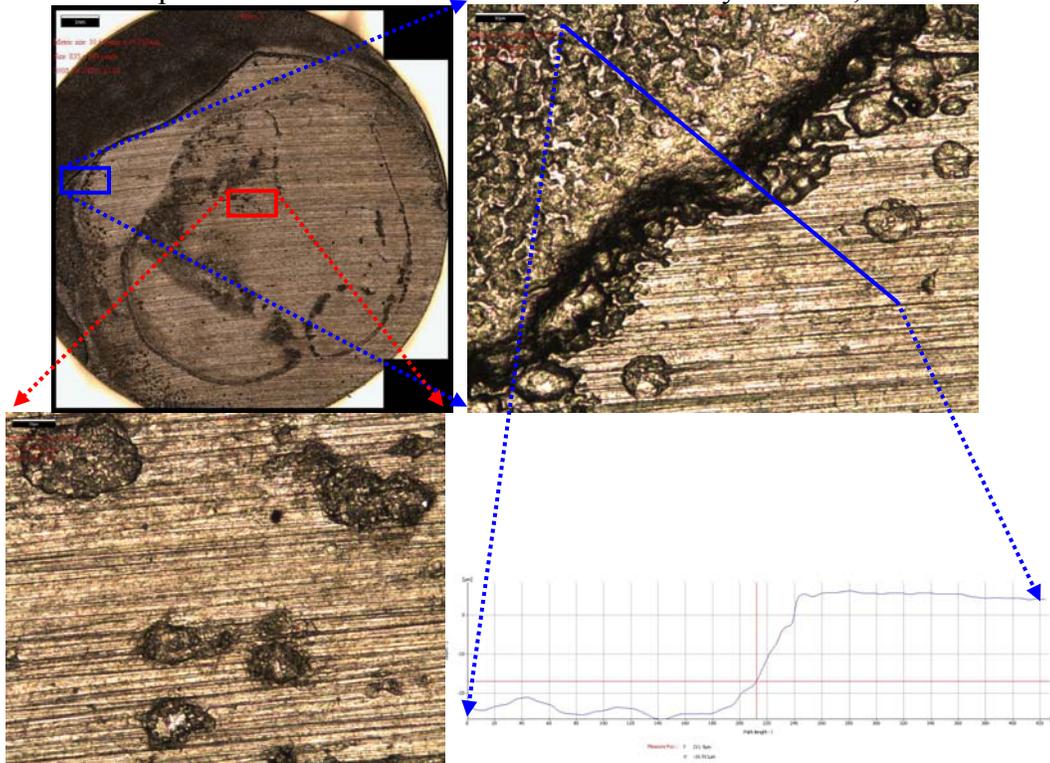
Figure 7. IFM data for coupon contacted with sulfur for 4 days at 25°C, without film, appearance of the surface and a line profile.
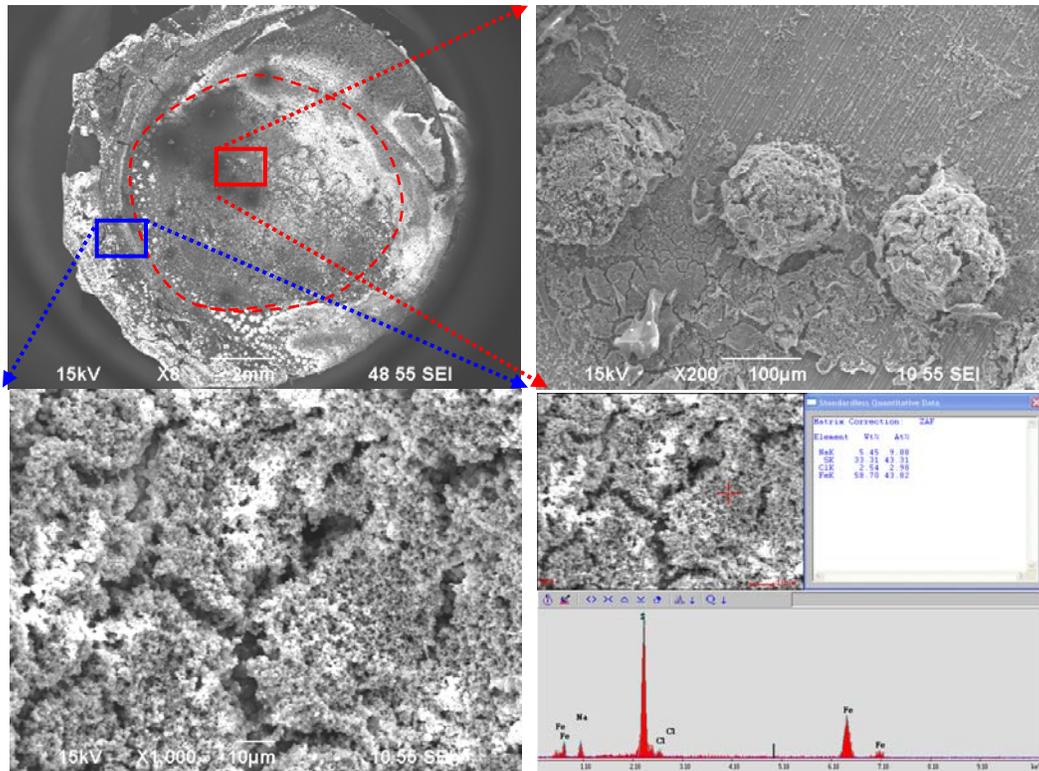
Figure 8. Corrosion coupon contacted with elemental sulfur for 5 days at 25°C, with film.
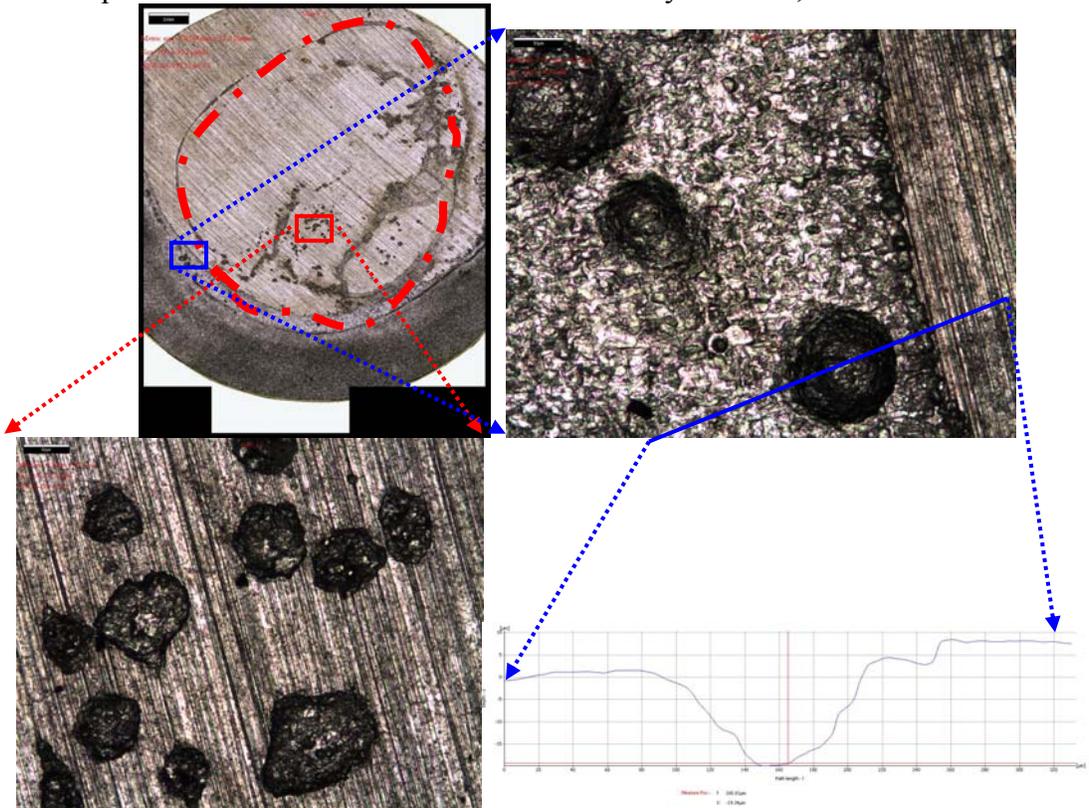
Figure 9. IFM data for coupon contacted with sulfur for 5 days at 25°C, without film, appearance of the surface and a line profile.

Figure 10. Corrosion coupon before and after 1 day exposure at 80°C.

Figure 11. Corrosion coupon before and after 4 days exposure at 80°C.

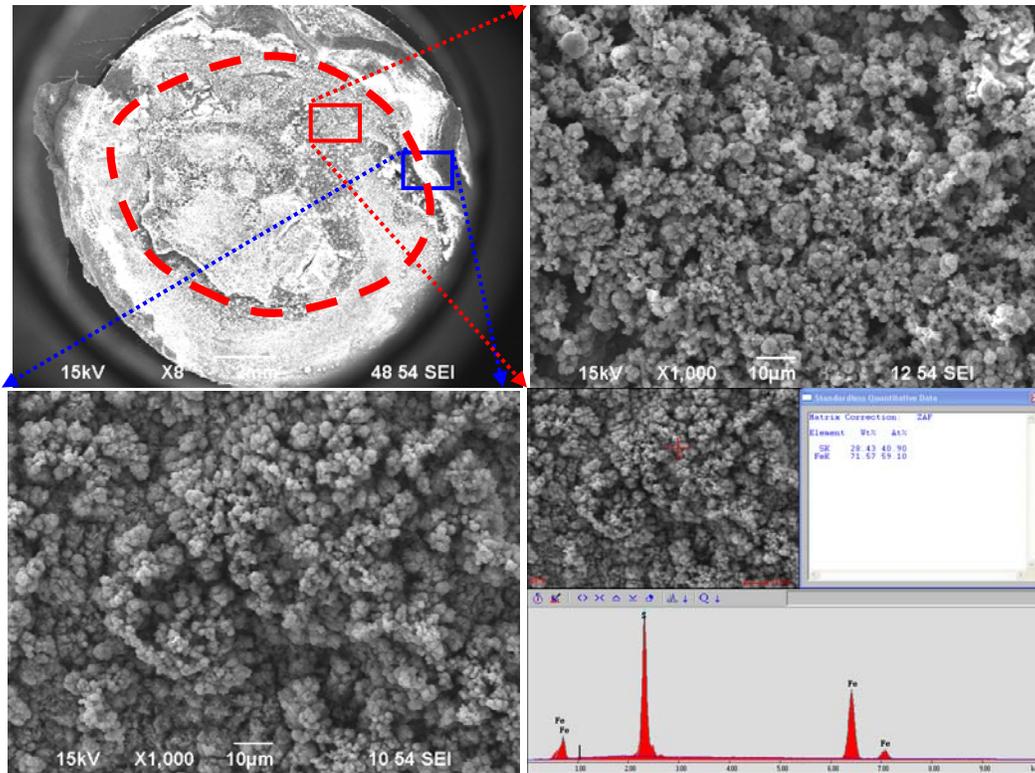Figure 12. Corrosion coupon before and after 5 days exposure at 80°C.

Figure 13. Corrosion coupon contacted with elemental sulfur for 1 day at 80°C, with film
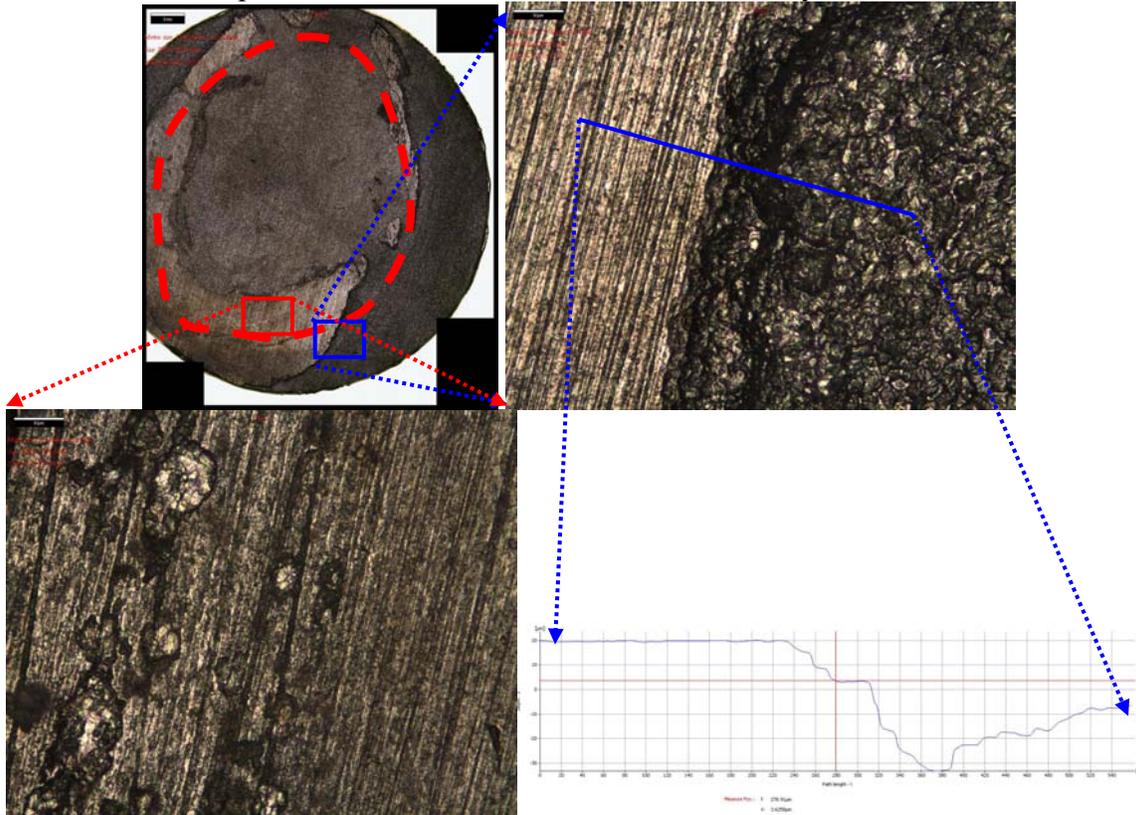

Figure 14. IFM data for coupon contacted with sulfur for 1 days at 80°C, without film, appearance of the surface and a line profile.
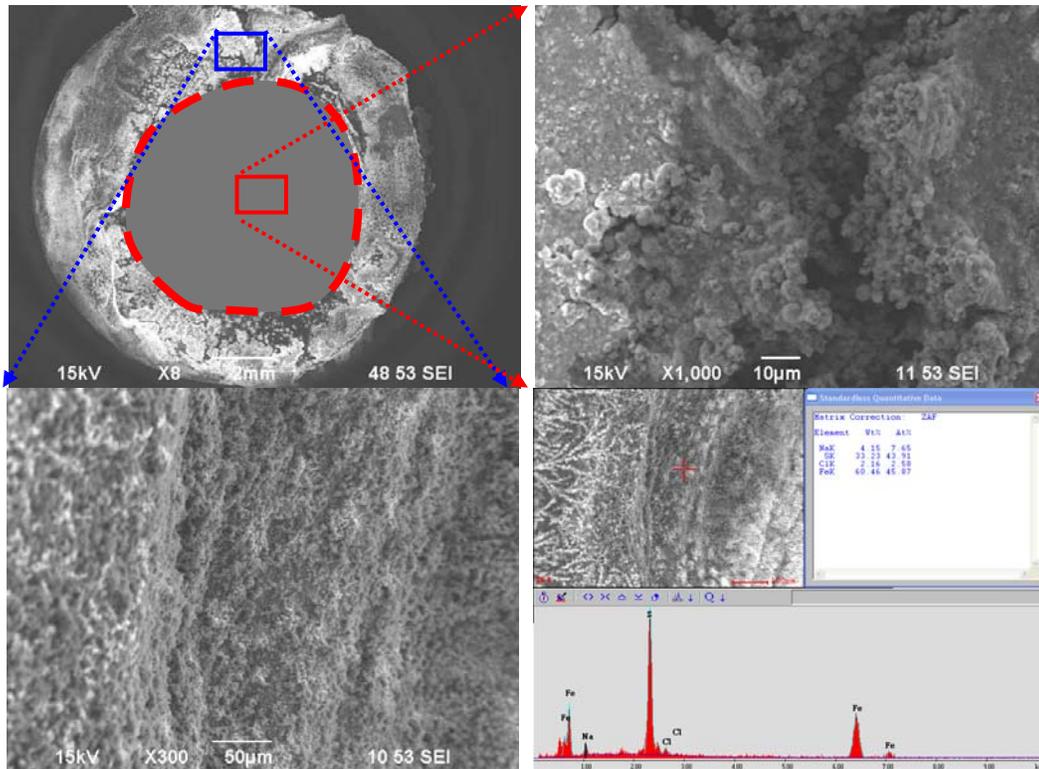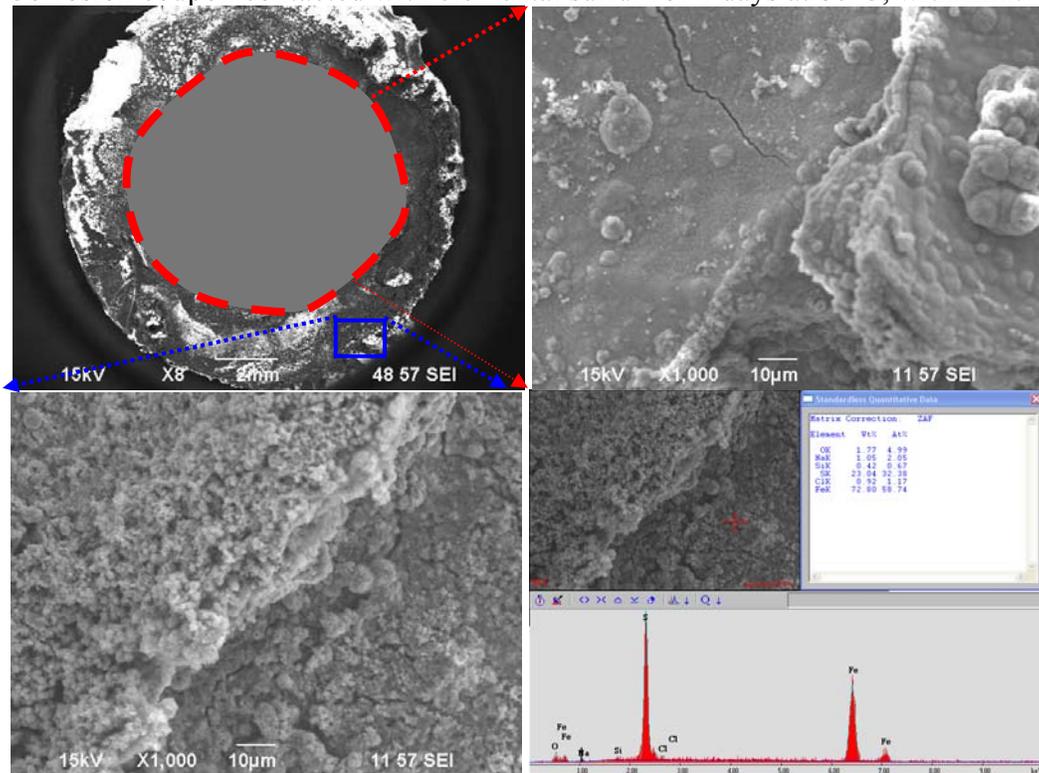
Figure 15. Corrosion coupon contacted with elemental sulfur for 4 days at 80°C, with film.

Figure 16. Corrosion coupon contacted with elemental sulfur for 5 days at 80°C, with film.
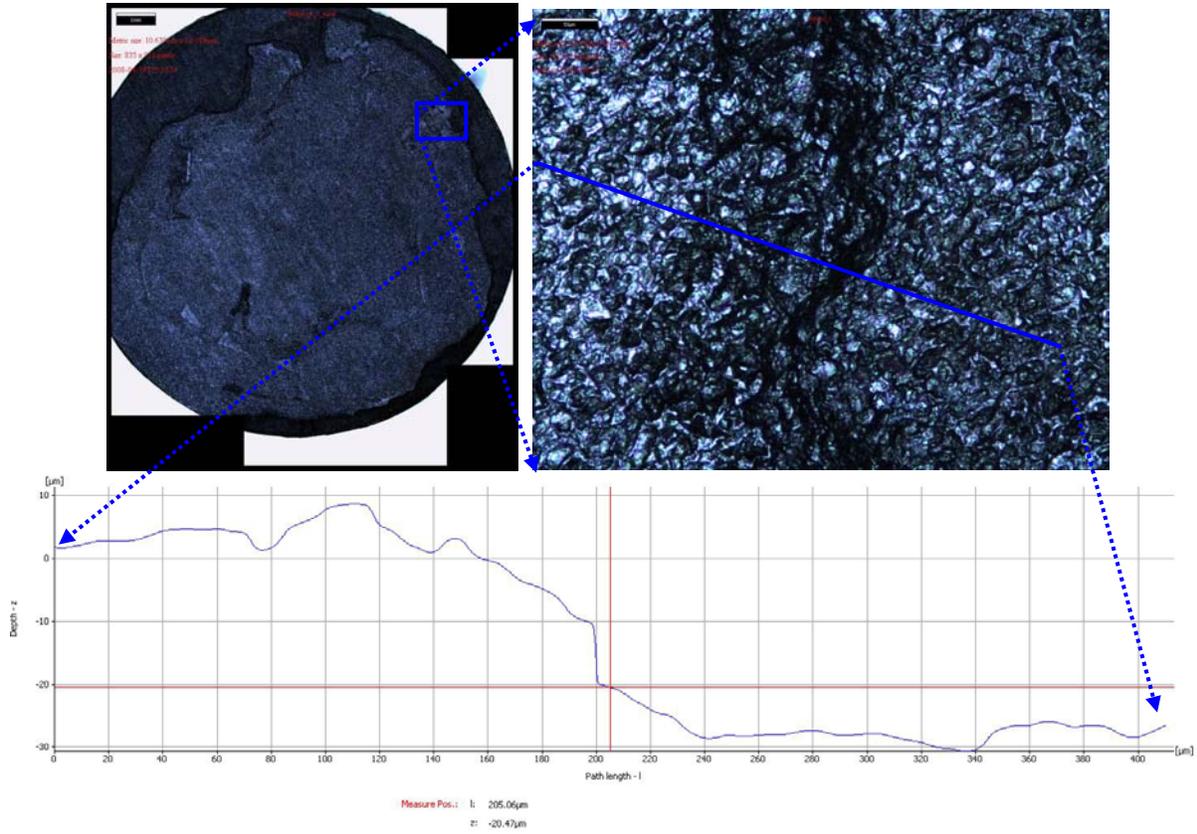
Figure 17. IFM data for coupon contacted with sulfur for 5 days at 80°C, without film, appearance of the surface and a line profile.
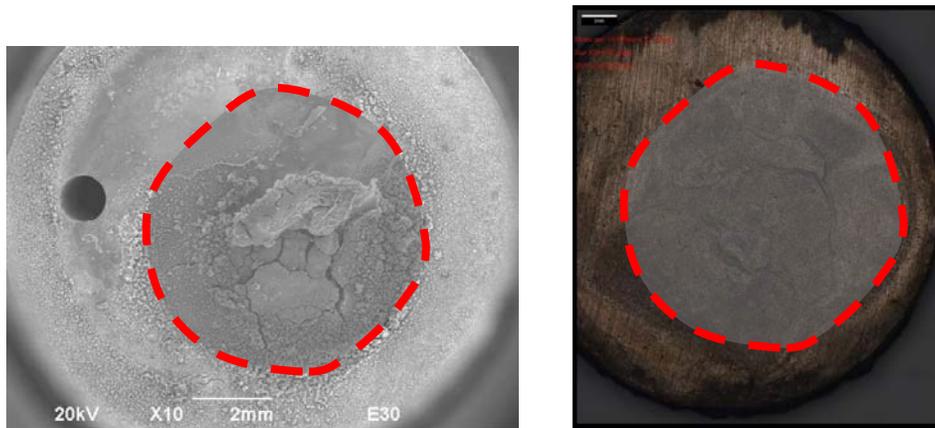

Figure 18. Corrosion coupon contacted with elemental sulfur for 4days with and without film at 25°C, salt free condition
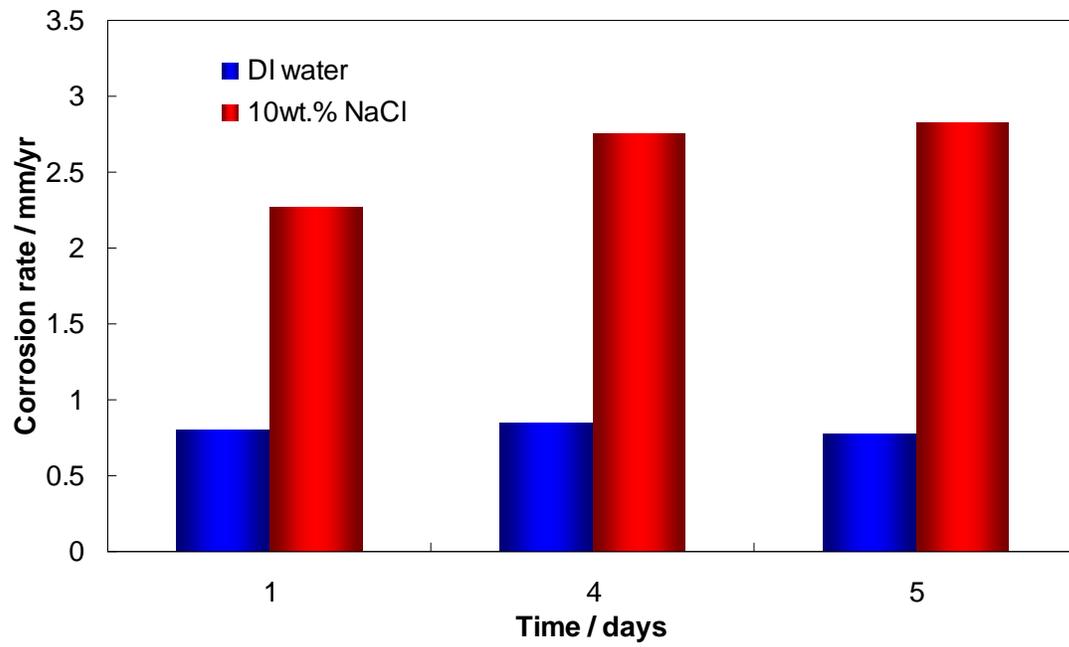
Figure 19. Comparisons of general corrosion between salt free and 10 wt.% NaCl conditions at 25°C.

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